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### **Methylene Bridging Effect on the Structures, Lewis Acidities and Optical Properties of SemiPlanar Triarylboranes**

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# Methylene Bridging Effect on the Structures, Lewis Acidities and Optical Properties of Semi-Planar Triarylboranes

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Dedicated to Professor Suzanne A. Blum

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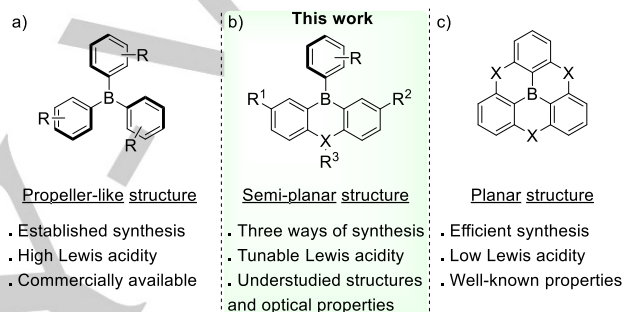
**Abstract:** Three synthetic methods towards semi-planar triarylboranes with two aryl rings connected by a methylene bridge have been developed. The fine-tuning of their stereoelectronic properties and Lewis acidities was achieved by introducing fluorine, methyl, methoxy, *n*butyl and phenyl groups either at their exocyclic or bridged aryl rings. X-ray diffraction analysis and quantum-chemical calculations provided quantitative information on the structural distortion experienced by the near planar hydro-boraanthracene skeleton during the association with Lewis bases such as  $\text{NH}_3$  and  $\text{F}^-$ . Though the methylene bridge between the *ortho*-positions of two aryl rings of triarylboranes decreased the Gibbs free energies of complexation with small Lewis bases by less than  $5 \text{ kJ mol}^{-1}$  relative to the classical Lewis acid  $\text{BAr}_3$ , the steric shielding of the  $\text{CH}_2$  bridge is sufficient to avoid the formation of Lewis adducts with larger Lewis bases such as triarylphosphines. A newly synthesized spirocyclic amino-borane with a long intramolecular B-N bond that could be dissociated under thermal process, UV-irradiation, or acidic conditions might be a potential candidate in Lewis pairs catalysis.

## Introduction

Owing to their unique chemical, physical and photophysical properties, trivalent organoboron compounds have become a mainstream interest in chemistry.<sup>[1]</sup> In particular, triarylboranes represent an invaluable class of Lewis acids, as demonstrated by their numerous applications in materials chemistry<sup>[2]</sup> and by their ability to catalyze a wide variety of transformations.<sup>[3]</sup>

Whereas typical triarylboranes possess a planar trigonal propeller-like structure (Scheme 1a), an enforced planarization of their aryl rings with three covalent linkers results in completely planar triarylboranes (Scheme 1c). These fully planar boron Lewis acids exhibit high chemical stability, low Lewis acidity, and are air, moisture, and chromatography compatible. They have recently found widespread applications in anions sensing, optoelectronic devices and boron doped  $\pi$ -conjugated materials.<sup>[4]</sup>

In contrast, the structures, reactivities and stereoelectronic properties of highly functionalized semi-planar triarylboranes with a single methylene bridge between two aryl rings have been less explored (Scheme 1b).<sup>[5]</sup>

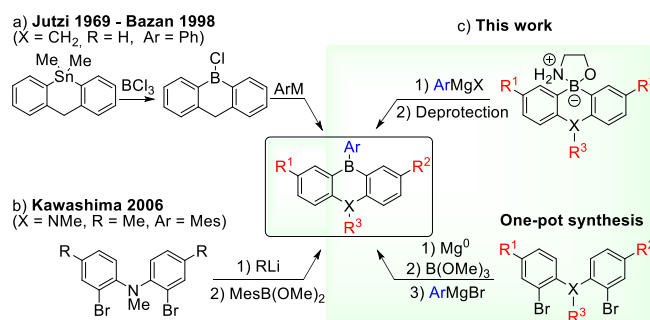


**Scheme 1.** From propeller-shaped to fully planar triarylboranes.

In contrast to the well-established synthetic methods to produce common triarylboranes  $\text{Ar}_3\text{B}$ ,<sup>[6]</sup> only few synthetic routes toward semi-bridged triarylboranes are known (Scheme 2).

Previous methods to produce semi-planar triarylboranes were mostly based on the introduction of the boron atom via a transmetalation of an organo-stannane or -silane in the presence of  $\text{BCl}_3$  or  $\text{BBr}_3$  (Scheme 2a).<sup>[5a-d]</sup> Another approach is based on a cyclization between a pre-functionalized arylboronate  $\text{FG-Ar-B(OR)}_2$  and a bis-organolithium intermediate which tolerates only a limited number of functionals groups (FG).<sup>[5e-g]</sup>

We now describe three synthetic methods towards functionalized semi-planar triarylboranes (Scheme 2c) and report the evaluation of their Lewis acidity, stereoelectronic and photophysical properties.



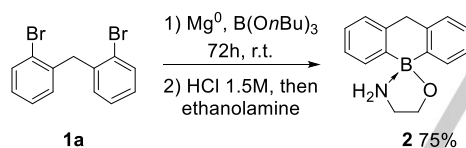
**Scheme 2.** Reported synthesis and our approach to the semi-cyclic boranes with different substituents on hydro-boraanthracene scaffold and different aryl rings attached to boron atom.

Experimental investigations combined with quantum chemical calculations of their associations with Lewis bases of various sizes and natures (halides, amines, phosphines) shed light on their steric properties and Lewis acidities, providing insights on their potential uses in chemical catalysis (frustrated Lewis pairs) and materials sciences (anion and Lewis base sensors).

## Results and Discussion

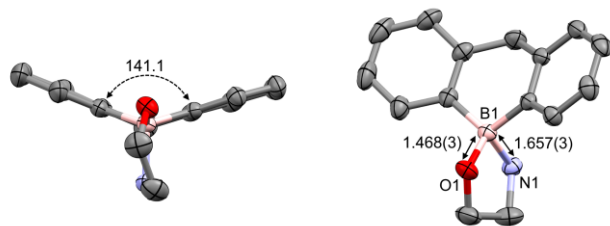
In order to avoid air and moisture sensitive halogeno-borane intermediates, we envisaged a practical access to semi-planar arylboranes *via* a water tolerant precursor **2** (Scheme 3). To the best of our knowledge only few boranes were synthesized by this approach,<sup>[5b,7]</sup> but a methodological investigation of the scope of this synthetic approach was not reported so far.

The spirocyclic quaternary ethanolamino complex **2** was prepared by a one-pot borylative cyclization reaction starting from the bis(2-bromophenyl)-methane **1a** (Scheme 3). The formation of the bis-organomagnesium reagent derived from **1a** under Barbier conditions in the presence a trivalent boron electrophile B(OnBu)<sub>3</sub>, followed by acidic treatment and addition of ethanolamine, produced **2** in 75% yield. With a shorter reaction time (16 h), an acceptable yield of 60% of **2** could be obtained (see the ESI). Despite of the purification of **2** by crystallization, some ethanolamine traces often remained in the final product, this can be avoided by reducing the amount of ethanolamine, however the yield was found to be lower (see the SI for details).



**Scheme 3.** Synthesis of the ethanolamine protected boronic acid **2**.

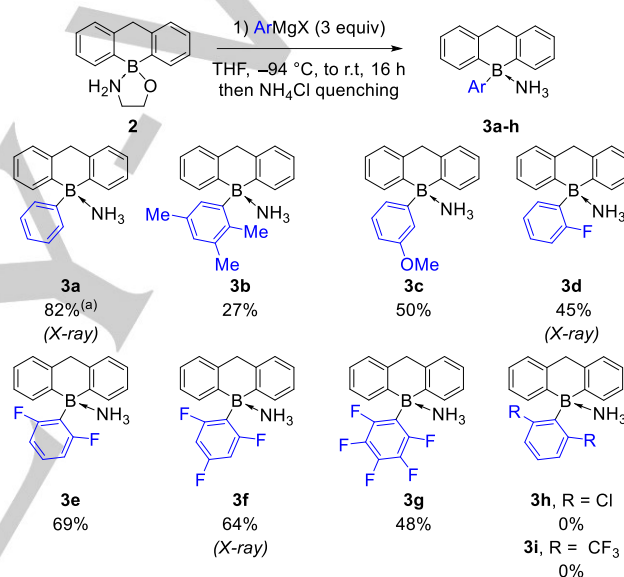
The X-ray diffraction analysis on a single-crystal of **2** showed a bent hydro-boraanthracene scaffold with an interplanar angle of 141.1° between two aryl rings (Figure 1). The value for the other asymmetric unit can be found in the ESI. The oxygen atom is located at the concave face of this tricyclic scaffold with the shorter B-O bond length (1.468(3) Å) compared to that in the non-bridged Ph<sub>2</sub>B(ethanolamine) adduct ((1.476(2) Å)<sup>[8a]</sup> and (1.484(3) Å)<sup>[8b]</sup>). The B-N bond length of 1.657(3) Å is similar to the bond lengths of 1.655(2) Å and 1.653(3) Å in the analogous non cyclic derivative Ph<sub>2</sub>B(ethanolamine).<sup>[8]</sup>



**Figure 1.** Molecular structure of compound **2** (one of the two in asymmetric unit, for the other unit, see the SI) with the selected interplanar angle (left) and B-N and B-O bond lengths (right). Here and further, thermal ellipsoids are shown at 50% probability level, hydrogen atoms non-involved in interactions and minor components of disorder are omitted for clarity.

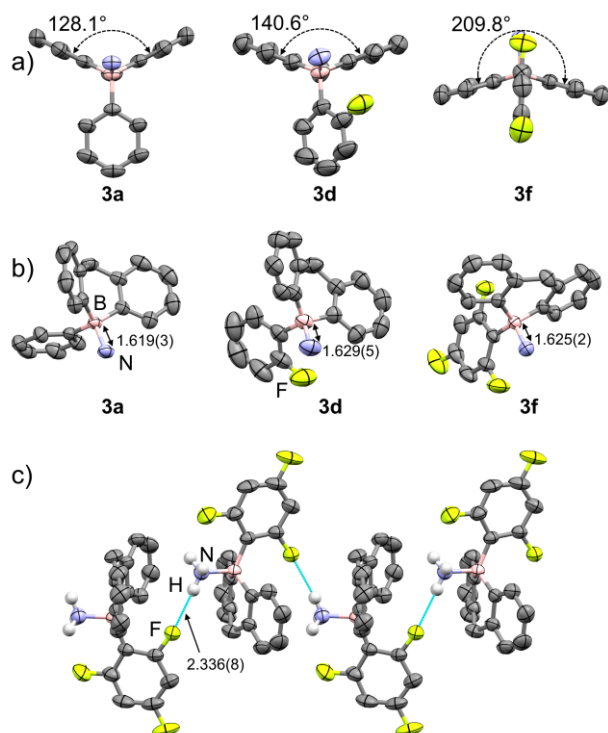
The formation of the ammonia protected triarylboranes **3a-g** via addition of various organomagnesium on the 9-aminoethoxy-9,10-dihydro-boraanthracene **2** was next investigated (Scheme 4). Our initial experimental conditions were based on an example reported by Shaver on a similar Ar<sub>2</sub>B(ethanolamine) derivative.<sup>[7b,7g]</sup>

Despite extensive reaction condition optimizations, the ammonia protected boranes **3a-g** were obtained with isolated yields in the 27-82% range. Increasing the excess of the organomagnesium reagents ArMgX up to 8 equivalents did not improve the yields further and the use of aryllithium reagents only produced the **3** in traces amounts. Despite of the moderate yields, the method was quite general and several *ortho*-substituents were tolerated (**3b**, **3d-g**), even the strongly electron deficient pentafluorophenyl-magnesium produced the pentafluorinated borane **3g** in 48% yield. As expected, di-*ortho*-trifluoromethyl or di-*ortho*-chloride substituents were not tolerated because of the excessive steric hindrance (**3h** and **3i**).



**Scheme 4.** Scope and limitation of the synthesis of ammonia-protected semi-cyclic triarylboranes **3a-i**. a) The addition of the Grignard reagent was performed at 0 °C instead of - 94 °C.

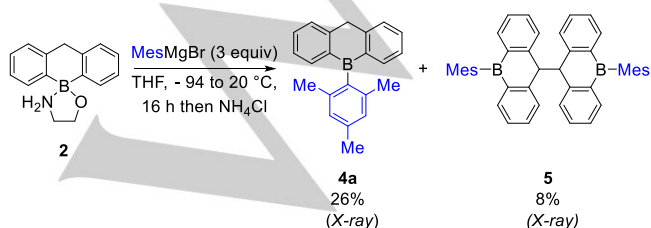
The interplanar angles between the mean planes of the two aryl rings of the bent hydro-boraanthracene skeleton in the triarylborane ammonia-complexes **3a**, **3d** and **3f** are 128.1°, 140.6° and 209.8°, respectively (Figure 2a). The smaller angle of **3a** compared to that of the spiro compound **2** (141.1°) is linked to the higher boron pyramidalization in **3a** (92%)<sup>[9]</sup> than in **2** (73%). The B-N bond lengths in **3a**, **3d** and **3f** are of 1.619(3), 1.629(5) and 1.625(2) Å, respectively (Figure 2b), slightly smaller than that of the Ph<sub>2</sub>B-NH<sub>3</sub> Lewis adduct (1.639(2) Å).<sup>[10]</sup>



**Figure 2.** Molecular structures of compound **3a**, **3d** and **3f** in two orientations (a) and b)), showing the dihedral angles between aryl rings and the B-N bond lengths. The intermolecular N-H...F interactions of **3f** (c)).

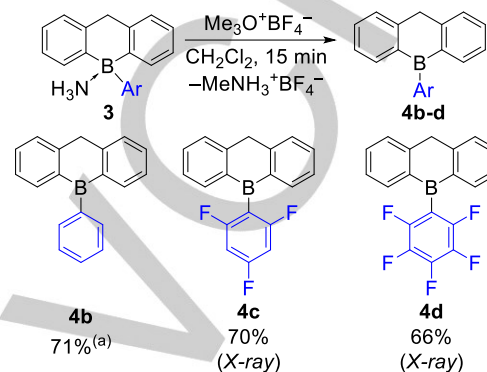
The exocyclic aryl rings in **3a** and **3d** are located in the convex face of the hydro-boraanthracene skeleton in a skewed fashion for maximizing van der Waals attractions with the peri-hydrogens of the hydro-boraanthracene motif. However, the aryl ring in **3f** is in a nearly perpendicular orientation (Figure 2a). Interestingly, the short intermolecular N-H...F interactions of 2.336(8) Å in **3f** (Figure 2c), which cannot be found in **3d**, reduce notably the exocyclic aryl ring twisting. In details, the C-C-B-N torsion angles of the *ortho*-fluorinated boranes **3d** and **3f** are 51.7° and 4.7°, respectively, which are significantly smaller than that of the non-fluorinated analogue **3a** (90.3°).

The same strategy was attempted to introduce the bulky mesityl group in the ammonia protected triarylborane system. However, no desired compound with the coordination between B atom and NH<sub>3</sub> was formed. In this case, the unprotected sterically hindered triarylborane **4a** was directly obtained, though in low yield together with the dimerization side product **5** (Scheme 5),<sup>[11]</sup> showing the limitations of this method with strongly hindered aryl Grignard reagents. The dimer **5** is presumably formed by oxidative homocoupling of two organomagnesium species or *via* a single-electron transfer between **4a** and MesMgBr.<sup>[12]</sup>



**Scheme 5.** Synthesis of the B-substituted mesityl semi-planarized borane **4a** and formation of the dimerization side-product **5**.

Removal of the coordinated ammonia from **3** was then performed in ethereal HCl or HBF<sub>4</sub> solutions,<sup>[7b]</sup> but we noticed partial degradation of the desired boranes by <sup>11</sup>B NMR measurements. In contrast, the methylation of NH<sub>3</sub> moiety with the Meerwein salt Me<sub>3</sub>O<sup>+</sup>BF<sub>4</sub><sup>-</sup> in CH<sub>2</sub>Cl<sub>2</sub> proceeded smoothly (Scheme 6), and filtration of the methyl-ammonium chloride salt provided the analytically pure triarylboranes **4b-d** as white crystalline solids in 66-71% isolated yields after solvent removal.



**Scheme 6.** Deprotection of ammonia-borane complexes **3** and formation of the free triarylboranes **4b-d**. (a) Due to the highly sensitive nature of **4b**, some impurities have been observed in the <sup>1</sup>H and <sup>13</sup>C NMR spectra (see the ESI for details).

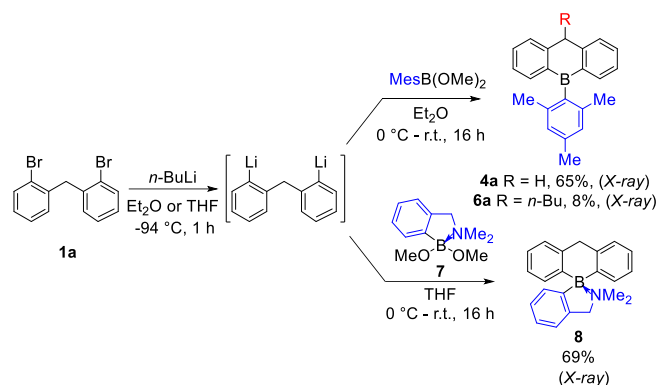
Although four semi-planar triarylboranes **4a-d** have been prepared, the long synthetic route and the limitations of the method for synthesizing the ammonia-protected triarylboranes with bulky aryl rings attached to the boron atom, are the disadvantages of the methodology.

In order to overcome these drawbacks, a straightforward method for introducing a mesityl group attached to boron atom has been developed (Scheme 7) based on the method of Kawashima (Scheme 2b). The synthesis pathway starts with the Br/Li exchange reaction of bis-(2-bromophenyl)-methane **1a** with *n*-BuLi, followed by the addition of mesityl(dimethoxy)borate MesB(OMe)<sub>2</sub> that was prepared from 2-bromomesitylene and trimethylborate, and was used directly without further purification (see the SI).

The desired compound **4a** was obtained in a yield of 65% and the side product **6a** with a *n*-butyl chain has been formed and its structure was confirmed by X-ray diffraction analysis (see the SI). Although the side product **6a** was formed, it was possible to perform the purification of the target compound **4a** by flash chromatography and also to isolate **6a** with a yield of 8%.

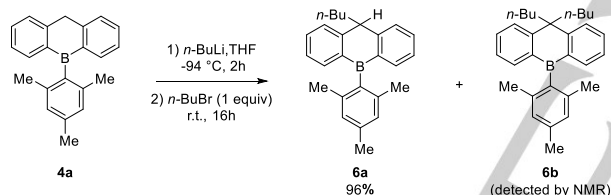
The same method was applied to synthesize the new spirocyclic amino hydro-boraanthracene **8** (Scheme 7). This compound was purified by crystallization from CH<sub>2</sub>Cl<sub>2</sub>/*n*-pentane at -20 °C due to its decomposition on SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>.





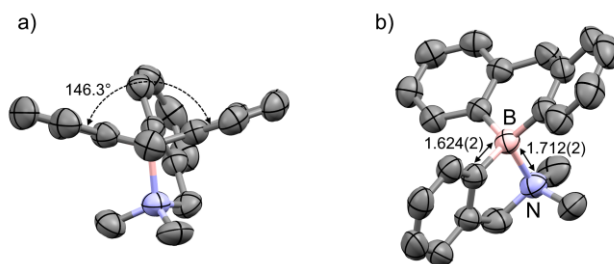
**Scheme 7.** Synthesis of the mesityl (**4a**) and the amino spirocyclic boraanthracene (**8**) derivatives by using organolithium reagent.

The formation of **6a** should result from the deprotonation of **4a** by an unreacted amount of  $n\text{-BuLi}$  followed by a nucleophilic substitution at the  $n\text{-butylbromide}$  released in the reaction during the  $\text{Br/Li}$  exchange on **1a**. This was confirmed by the independent synthesis of the semi-planar derivative **6a** with a yield of 96% (traces amount of **6b** have been detected) by deprotonation of **4a** and addition of  $n\text{-butylbromide}$ . This result shows that the functionalization at C9 position of mesityl-hydroantracenyloboranes can open an access to new semi-planar triarylboranes **6a** functionalized at the bridge (Scheme 8).



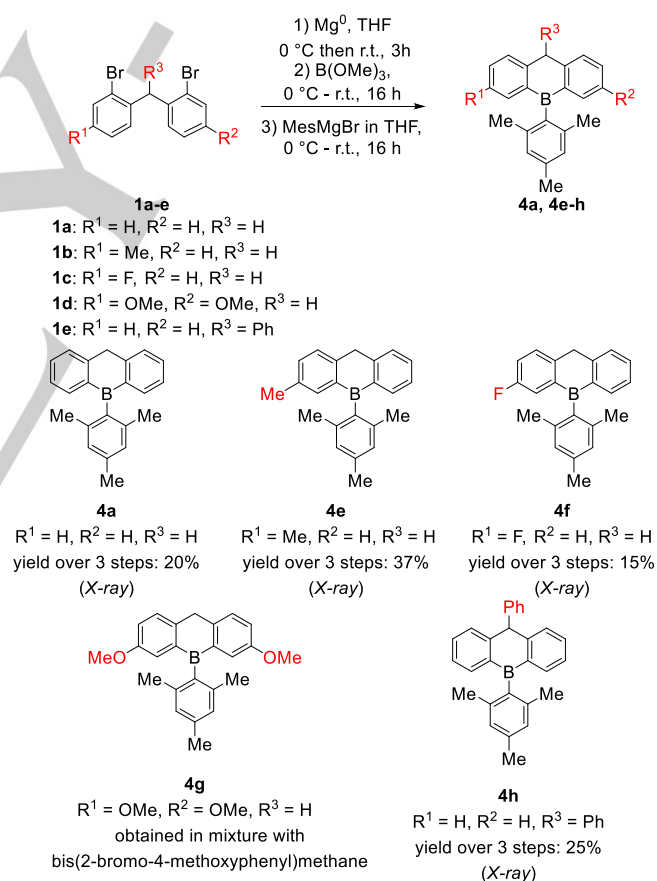
**Scheme 8.** Synthesis of functionalised semi-planar triarylboranes **6a** and **6b**.

The structure of **8** with the intramolecular B-N coordination was confirmed by X-ray diffraction analysis (Figure 3). The interplanar angle between two aryl rings of hydro-boraanthracene moiety is  $146.3^\circ$ . The B-N bond length of  $1.712(2) \text{ \AA}$  is consistent with a B-N coordination and is comparable to that of the similar systems containing the borafluorene scaffold instead of the boraanthracene skeleton ( $1.712(2) \text{ \AA}$  [13] and  $1.673(1) \text{ \AA}$  [14]). In comparison to the ethanolamine protected borinic acid **2** shown in Figure 1 with B-N bond length of  $1.657(3) \text{ \AA}$ , the B-N bond in compound **8** is longer. In addition, the bond length between B atom and the adjacent C atom of the five-membered ring is much longer than the B-O bond in the compound **2** ( $1.624(2) \text{ \AA}$  compared to  $1.468(3) \text{ \AA}$ ). These data reveal that the five-membered ring in the spirocyclic amino hydro-boraanthracene **8** is less stable than the five-membered ethanolamine ring in compound **2** and might be opened under thermal process, UV-irradiation, or acidic conditions.[15] By fine-tuning the electronic and structural properties of the boraanthracene scaffold and the Lewis base, this benchmark structure should find some applications in frustrated Lewis pair chemistry or bifunctional metal free catalysis.



**Figure 3.** Structure of compound **8** with the dihedral angle between aryl rings (left) and B-N bond length (right).

A third method was then developed to obtain mesityl-hydro-boraanthracenes by performing the successive reaction of two Grignard reagents on a boron electrophile in a one-pot fashion (Scheme 9). The bis-organomagnesium reagent produced by the reaction between **1a** and  $\text{Mg}^0$  was reacted with trimethylborate, followed by the addition of  $\text{MesMgBr}$  to give **4a** with the yield of 20%.



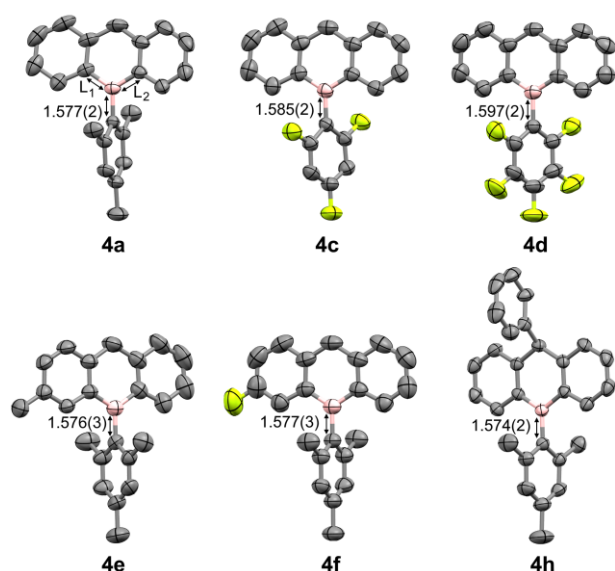
**Scheme 9.** One-pot method to reach mesityl-hydro-boraanthracenes **4a-h** by successive addition of two Grignard reagents.

Based on this method, the introduction of different substituents like methyl or fluoride in one side of the hydro-boraanthracene skeleton has been applied successfully to give **4e** and **4f** in the yields of 37% and 15%, respectively. The insertion of two methoxy groups was also possible, however, the pure

compound **4g** was not obtained due to the same  $R_f$  with the formed bis-(2-bromo-4-methoxyphenyl)methane side product.

In addition, this method also worked well with the starting material **1e** containing a phenyl group at the benzylic position to produce **4h** in the yield of 25%, and analogue of **6a**.

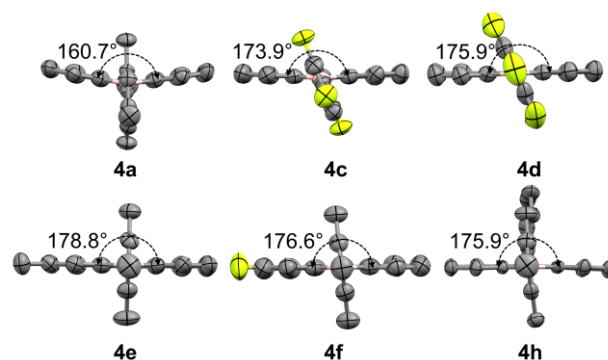
The X-ray diffraction crystallographic structures of compounds **4a**, **4c-f** and **4h** are shown in Figure 4. The structure of **4h** was also previously reported in the literature.<sup>[16]</sup> Considering **4a**, **4e**, **4f** and **4h** having the mesityl ring attached to the B atom, the similar bond lengths in the range of 1.543 – 1.546 Å between B atom and the adjacent C atoms of the hydro-boraanthracene skeletons as well as the similar distances in the range of 1.574 – 1.577 Å between B atom to the mesityl moiety show the minor effects of substituents on B-C bonds length. The distances from B atom to the mesityl ring of **4a**, **4e**, **4f** and **4h** are similar to the same distance of 1.575(3) Å in 9-phenyl-hydro-boraanthracene **4b**.<sup>[17]</sup> The longer distances in the cases of **4c** and **4d** compared to **4a** (1.585(2) and 1.597(3) Å vs 1.577(2) Å, respectively) exhibit the effect of F atom on the structures. The more the number of fluorine atoms, the longer B-C distances have been obtained.



**Figure 4.** Structures of compounds **4a**, **4c-f** and **4h** with the selected B-C bond lengths. Selected bond lengths  $L_1$  and  $L_2$  in Å for **4a**: 1.546(2) and 1.544(2); **4c**: 1.537(3) and 1.536(3); **4d**: 1.525(3) and 1.533(3); **4e**: 1.543(3) and 1.550(3); **4f**: 1.543(2) and 1.543(2); and **4h**: 1.544(2) and 1.545(2), respectively.

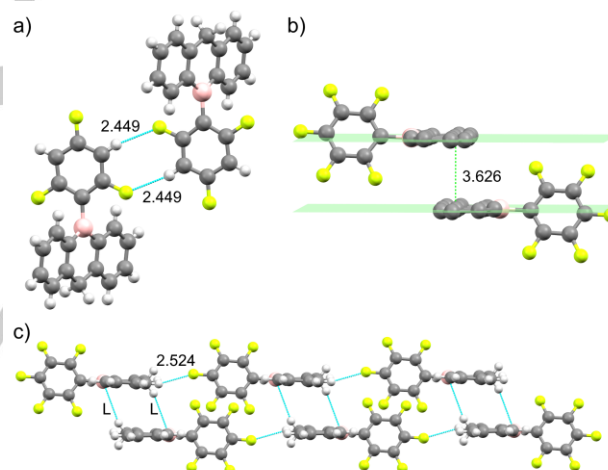
The hydro-boraanthracene skeleton in **4c-f** and **4h** are almost planar as shown by the angles between two aryl rings of 173.9°, 175.9°, 178.8°, 176.6° and 175.9°, respectively (Figure 5). Compound **4a** is the most bent hydro-boraanthracene structure with the corresponding angle of 160.7°.

The mesityl moieties in **4a**, **4e** and **4h** are almost perpendicular to the hydro-boraanthracene scaffold with the corresponding angles of 87.8°, 88.2° and 84.9°, respectively. The presence of fluoride leads to the rotation of aryl rings attached to the B atom. In details, **4f** containing one fluoride substituent has the rotated angle of 83.5°, while **4c** and **4d** bearing three and five fluorides on the aryl rings show the most twisted angles of 67.1° and 66.8°, respectively.



**Figure 5.** Molecular structures of compounds **4a**, **4c-f** and **4h** with the selected dihedral angles.

This difference in terms of rotation angles in the case of **4c** and **4d** are potentially due to H··F intermolecular interactions between two nearby molecules with distances of 2.449 Å and 2.524 Å, respectively (Figures 6a and 6c). Interestingly, face-to-face stacking between the parallel hydro-boraanthracene units exists in the structure of **4d** in the solid state with an interplanar distance of 3.626 Å (Figure 6b).

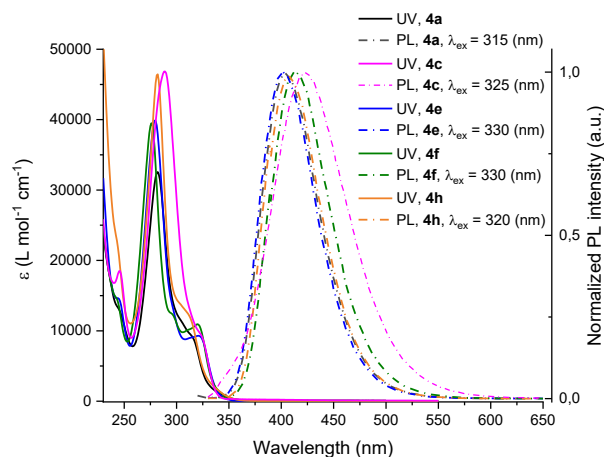


**Figure 6.** a) The intermolecular H··F interactions in the structure of **4c**; b) the interplanar distance between two parallel hydro-boraanthracene units of **4d**; c) the intermolecular H··F interactions and the face-to-face stacking between the hydro-boraanthracene units in the structure of **4d**. Atoms are shown in ball-and-stick representation.

The UV/Vis absorption and photoluminescence (PL) spectra of **4a**, **4c**, **4e**, **4f** and **4h** in  $\text{CH}_2\text{Cl}_2$  are presented in Figure 7. Their spectroscopic data are listed in Table 2.

The bridged triarylborane **4c** containing three F atoms displays the most pronounced red-shifted absorption and emission spectra with  $\lambda_{\text{Abs, max}} = 324$  and 289 nm, and  $\lambda_{\text{PL, max}} = 424$  nm. The slightly bathochromic shifted spectra of **4c** compared to that of **4a** (with  $\lambda_{\text{Abs, max}} = 315$  and 282 nm and  $\lambda_{\text{PL, max}} = 405$  nm) show the insignificant effect of different groups on exo-aryl ring on photophysical behaviors. Similar minor effect was obtained when changing different substituents (Me and F) in the cases of

**4e** and **4f**, or adding phenyl group at the benzylic position in **4h**. The appearance of absorbance bands at longer wavelength for these five compounds compared to that of  $\text{Ph}_3\text{B}$  ( $\lambda_{\text{Abs, max}} = 287$  nm in methylcyclohexane/isopentane)<sup>[18]</sup> underlines the role of methylene bridge in the extent of  $\pi$ -delocalization by imposing the planarization of the system and enhancing the conjugation of the aryl rings through the boron atom.



**Figure 7.** UV/Vis (solid line) and photoluminescence (PL) (dashed line) spectra of the synthesized semi-planar triarylboranes **4a**, **4c**, **4e**, **4f** and **4h** in  $\text{CH}_2\text{Cl}_2$ .

**Table 2:** Spectroscopic data of the semi-planar triarylboranes **4a**, **4c**, **4e**, **4f** and **4h** in  $\text{CH}_2\text{Cl}_2$ .

Comp.	$\lambda_{\text{Abs max}}$ (nm)	$\epsilon$ ( $\text{L mol}^{-1} \text{cm}^{-1}$ )	$\lambda_{\text{PL max}}$ (nm)	Stokes shift ( $\text{cm}^{-1}$ )
<b>4a</b>	315 <sup>[a]</sup>	9180	405	7060
	282	32570	(at $\lambda_{\text{ex}} = 315$ nm)	
	245 <sup>[a]</sup>	13050		
<b>4c</b>	324 <sup>[a]</sup>	9240	424	7280
	289	46850	(at $\lambda_{\text{ex}} = 325$ nm)	
	246	18500		
<b>4e</b>	321	9300	402	6280
	279	39870	(at $\lambda_{\text{ex}} = 330$ nm)	
	245 <sup>[a]</sup>	14530		
<b>4f</b>	320	10940	414	7100
	297 <sup>[a]</sup>	12150	(at $\lambda_{\text{ex}} = 330$ nm)	
	276	39500		
	244 <sup>[a]</sup>	14120		
<b>4h</b>	313 <sup>[a]</sup>	11870	408	7440
	282	46450	(at $\lambda_{\text{ex}} = 320$ nm)	

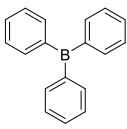
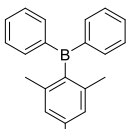
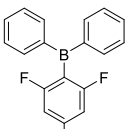
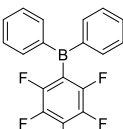
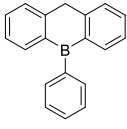
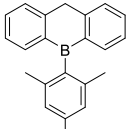
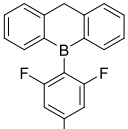
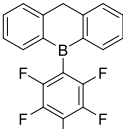
<sup>[a]</sup>: shoulder.

Interestingly, large Stokes shifts were observed in all cases, ranging from 6280 to 7440  $\text{cm}^{-1}$ . The presence of the weak electron donating methyl group at position 7 of the 9-hydro-boraanthracene skeleton in **4e** leads to a strong decrease of 780  $\text{cm}^{-1}$  of the Stokes shift compared to **4a**, whereas in the case of **4f**, fluoride as the weak electron withdrawing group at the same position makes a minor difference of 40  $\text{cm}^{-1}$ . The highest value of 7440  $\text{cm}^{-1}$  associated to **4h** proves the role of phenyl group at the position 10 of the 9-hydro-boraanthracene skeleton in

increasing intramolecular charge transfer in the system. Surprisingly, these Stokes shifts are comparable to the value of 6680  $\text{cm}^{-1}$  of the fully planarized triarylboranes measured in THF and reported by Yamaguchi, and nearly double compared to the value of 3380  $\text{cm}^{-1}$  of  $\text{Mes}_3\text{B}$  with a typical propeller-like structure.<sup>[19]</sup>

We next determined the Lewis acidities of selected semi-planar triarylboranes **4** with respect to various Lewis bases by calculating their fluoride anion affinities (FIAs) and  $\text{NH}_3$  affinities, which are well-established Lewis acidity scales for comparing extensive sets of Lewis acids, due to the small size of these Lewis bases which result in negligible influence of sterics on the acidity measurements.<sup>[20]</sup> The  $\text{F}^-$  and  $\text{NH}_3$  affinities computed at the M06-2X/6-311G(d) level of theory (Scheme 10) showed that the introduction of a methylene bridge has a negligible influence on the Lewis acidity of the boron atom since the  $\text{F}^-$  or  $\text{NH}_3$  affinities of **4b** are only 4  $\text{kJ mol}^{-1}$  smaller than those of triphenylborane **9a**. Furthermore, the evaluation of the global and local electrophilicity indexes also indicated a slight decrease of acidity upon addition of a methylene bridge.<sup>[21]</sup> Increasing the number of fluorine atoms on the exocyclic aryl ring expectedly increased the Lewis acidity of the boron atom, as illustrated by an increase of FIA amplitude of almost 40  $\text{kJ mol}^{-1}$  for **4d** ( $\text{Ar} = \text{C}_6\text{F}_5$ ) versus **4b** ( $\text{Ar} = \text{Ph}$ ).

In addition, the  $\Delta G^\theta$  of association of the mesityl-borane **4a** with  $\text{NH}_3$  is nearly equal to 0  $\text{kJ mol}^{-1}$ , which is in full agreement with the experimental observation that the Lewis adduct between **4a** and ammonia was not formed (Scheme 10). In agreement with the experimentally reported formation of the  $\text{Ph}_3\text{P} \cdot \text{BPh}_3$  Lewis adduct,<sup>[22]</sup> the Gibbs free energy of association of the large Lewis base  $\text{PPh}_3$  with  $\text{BPh}_3$  **9a** was found to be negative ( $\Delta G^\theta = -7$   $\text{kJ mol}^{-1}$ ). The association of  $\text{PPh}_3$  with the semi-planar borane **4b** is however thermodynamically unfavorable ( $\Delta G^\theta = +20$   $\text{kJ mol}^{-1}$ , Scheme 10). Since **4b** is as Lewis acidic as  $\text{BPh}_3$  **9a**, it highlights that the presence of the methylene bridge in **4b** strongly shields the boron atom and prevents the system from conformational changes that would reduce the steric repulsions, thus resulting in a frustrated Lewis pair.<sup>[23]</sup>

				
	<b>9a</b>	<b>9b</b>	<b>9c</b>	<b>9d</b>
<b>F<sup>-</sup></b>	-333 (174)	-324 (135)	-353 (159)	-379 (159)
<b>NH<sub>3</sub></b>	-43 (74)	-19 (89)	-63 (92)	-67 (91)
<b>PPh<sub>3</sub></b>	-7 (69)	40 (92)	-3 (93)	8 (103)
<b>ω</b>	1.53	1.43	1.68	1.86
<b>ω<sub>B</sub></b>	-0.65	-0.69	-0.74	-0.81
				
	<b>4b</b>	<b>4a</b>	<b>4c</b>	<b>4d</b>
<b>F<sup>-</sup></b>	-333 (169)	-306 (141)	-349 (176)	-372 (179)
<b>NH<sub>3</sub></b>	-39 (107)	0 (95)	-55 (102)	-58 (102)
<b>PPh<sub>3</sub></b>	20 (136)	43 (100)	31 (159)	-5 (97)
<b>ω</b>	1.48	1.38	1.61	1.77
<b>ω<sub>B</sub></b>	-0.61	-0.63	-0.67	-0.73

**Scheme 10.** M06-2X/6-311G(d) gas phase fluoride ion affinities (FIA,  $\Delta H^\circ$  in kJ mol<sup>-1</sup>), affinities with ammonia and triphenylphosphine (Gibbs free energies,  $\Delta G^\circ$  in kJ mol<sup>-1</sup>), global ( $\omega$ , in eV) and local (boron,  $\omega_B$ , in eV) electrophilicity indexes of the borane derivatives **9a-d** and **4a-d**. As a comparison, the corresponding affinities (in kJ mol<sup>-1</sup>) of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> for F<sup>-</sup> ( $\Delta H^\circ$ ), NH<sub>3</sub> ( $\Delta G^\circ$ ) and PPh<sub>3</sub> ( $\Delta G^\circ$ ) are -466, -117 and -62 respectively while its global and local electrophilicity indexes are respectively 2.79 eV and -1.23 eV.<sup>[24]</sup> In parenthesis are indicated the reorganization energies necessary for the borane to reach its final geometry in the Lewis adduct.

## Conclusion

Three synthetic methods towards semi-planar triarylboranes have been developed. Four semi-planar triarylboranes with phenyl, mesityl and fluoroaryl moieties attached to boron atom, six functionalized mesityl-hydro-boraanthracenes and one spirocyclic amino-borane derivative have been synthesized successfully by these methods.

The fine-tuning of the triarylboranes stereoelectronic properties and Lewis acidities was achieved by introducing fluorine, methyl, *n*-butyl, phenyl and methoxy groups either on their exocyclic aryl ring, bridged aryl rings, or methylene bridge. First, the photophysical properties of these semi-planar triarylboranes have been systematically evaluated. The presence of different substituents displays a minor effect on the UV-Vis and PL spectra, whereas the introduction of a methylene bridge at *ortho*-position induces a large Stokes shift in the similar range of the planar triarylboranes described by Yamaguchi.

Next, X-ray crystallographic analysis, NMR investigations and DFT calculations showed that the covalent methylene bridge connecting two aryl rings of these boranes by their *ortho*-positions has a strong effect on their structural flexibility, and on the steric shielding around the boron atom, though their Lewis acidity is nearly unaffected as shown by the respective energies of associations with the small NH<sub>3</sub> and F<sup>-</sup> Lewis bases in comparison with those of BPh<sub>3</sub>. The steric shielding of the boron atom by the methylene bridge in *ortho*-position is shown to

preclude Lewis acid-base adduct formation with triarylphosphines. These Lewis acid/base pairs and the newly synthesized spirocyclic amino-borane might be potential candidate in frustrated Lewis pair catalysis due to their weak B-P and B-N bonds, which should dissociate under thermal process, UV-Vis irradiation, or acidic conditions.

## Experimental Section

Experimental procedures for the synthesis of the final compounds and intermediates as well as their characterizations, NMR spectra, UV/Vis and photoluminescence spectra, DFT calculations and crystallographic data are described in detail in the Supporting Information.

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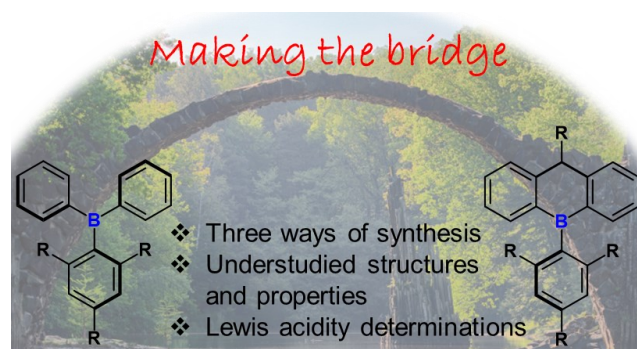
**Keywords:** semi-planar triarylboranes • boron Lewis acidity • Lewis adduct • structure property relationship

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## Entry for the Table of Contents



A series of semi-planar triarylboranes were obtained by three procedures. The effects of the planarization induced by the methylene bridge on their steric shielding, Lewis acidities and optical properties have been investigated by experiments and quantum chemical calculations. These methods can be extended to the preparation of functionalized spirocyclic amine-boranes and unsymmetrical triarylboranes, which might be used in frustrated Lewis pair chemistry or as pH and photo-responsive boron Lewis acids.

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